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Phase Composition Study of Corrosion Products at NPP

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1. Introduction

Corrosion at nuclear power plants (NPP) is a problem which is expected. If it is managed properly during the whole NPP lifetime, consequences of corrosion processes are not dramatic. For adequate protection against corrosion it is important to collect all relevant parameters including exact phase composition of registered corrosion products.

Corrosion is more frequent and stronger in secondary circuit of NPP. Steam generator (SG) is generally one of the most important components from the corrosion point of view at all NPP with close impact to safe and long-term operation. Various designs were developed at different NPPs during last 50 years. Wide type of steels was used in respect of specific operational conditions and expected corrosion processes. In our study we were focused on the Russian water cooled and water moderated reactors (VVER). These reactors are unique because of horizontal position of SGs. It takes several advantages (large amount of cooling water in case of loss of coolant accident, good accessibility, large heat exchange surface, etc. ...) but also some disadvantages, which are important to take into account during the operation and maintenance. Material degradation and corrosion/erosion processes are serious risks for long-term reliable operation. In the period of about 10-15 year ago, the feed water pipelines were changed at all SG in all 4 Bohunice units (V-1 and V-2, in total at 24 SGs). Also, a new design of this pipeline system was performed. Actually, there is a time to evaluate the benefit of these changes.

The variability of the properties and the composition of the corrosion products of the stainless Cr-Ni and mild steels in dependence on the NPP operating conditions (temperature, acidity, etc.) is of such range that, in practice, it is impossible to determine the properties of the corrosion products for an actual case from the theoretical data only. Since the decontamination processes for the materials of the VVER-440 secondary circuits are in the progress of development, it is necessary to draw the needed information by the measurement and analysis of the real specimens [1].

2. Mössbauer spectroscopy advantages

The phenomenon of the emission and absorption of a γ -ray photon without energy losses due to recoil of the nucleus and without thermal broadening is known as the Mössbauer

effect. Its unique feature is in the production of monochromatic electromagnetic radiation with a very narrowly defined energy spectrum that allows resolving minute energy differences [2,3].

Mössbauer spectroscopy (MS) is a powerful analytical technique because of its specificity for one single element and because of its extremely high sensitivity to changes in the atomic configuration in the near vicinity of the probe isotopes (in this case ^{57}Fe). MS measures hyperfine interactions and these provide valuable and often unique information about the magnetic and electronic state of the iron samples, their chemical bonding to co-ordinating ligands, the local crystal symmetry at the iron sites, structural defects, lattice-dynamical properties, elastic stresses, etc. [1,4]. Hyperfine interactions include the electric monopole interaction, i.e., the isomer shift, the electric quadrupole interaction, i.e., the quadrupole splitting, and the magnetic dipole (or nuclear Zeeman) interaction, i.e., hyperfine magnetic splitting. These interactions often enable us detailed insight into the structural and magnetic environment of the Mössbauer isotope. Indeed, more than four decades after its discovery (1958), Mössbauer spectroscopy still continues to develop as a sophisticated scientific technique and it is often the most effective way of characterizing the range of structures, phases, and metastable states.

In general, a Mössbauer spectrum shows different components if the probe atoms are located at lattice positions, which are chemically or crystallographically unequivalent. From the parameters that characterise a particular Mössbauer sub-spectrum it can, for instance, be established whether the corresponding probe atoms reside in sites which are not affected by structural lattice defects, or whether they are located at defect-correlated positions. Each compound or phase, which contains iron, has typical parameters of its Mössbauer spectrum. It means, the method is suitable for quantitative as well as qualitative analysis. Mössbauer spectroscopy is non-destructive and requires relative small quantities of samples (~100 mg) [5-8].

Application of Mössbauer spectroscopy for precise analysis of phase composition of corrosion products was performed from selected areas of primary and secondary circuit and SG. Interpretation of measured results, having in vision the long-term operation and nuclear safety, is not easy, nor straightforward. Thanks to our more than 25 years of experiences in this area, there exists already a base for the relevant evaluation of results. Optimisation of operating chemical regimes as well as regimes at decontamination and passivation seems to be an excellent output.

3. Safety analyses of Slovak steam generators and latest upgrades

The safe and reliable operation of steam generators is the essential pre-condition for the safe operation of the whole NPP, but also for all economical parameters at the unit. The steam generator has to be able to transfer the heat from the reactor in all operating or accidental regimes.

It is well-known that VVER-440 units have the horizontal steam generators with much higher capacity of cooling water in tank than in vertical steam generators, which are normally used in western NPPs. Undoubtedly; these horizontal steam generators are safer. On the other hand, due to horizontal design as well as in total 6 loops with additional welds and pumps cover a huge area, which is a limiting factor for containment construction of the

unit. The exchange of steam generators is extremely difficult (in some reactor types almost impossible), therefore their optimal operation and clever maintenance (upgrades) is one of essential duty of NPP staff.

Based on operational experiences, the mitigation of damages and leak tightness defects in pipelines or collectors require much more time and money, than prevention measures. It is necessary to keep in mind the actual development in nuclear industry towards NPP lifetime prolongation and power increase (one of essential goals of European Commission 7FP-NULIFE). Fortunately, VVER-440 steam generators were designed with the huge power reserve (possible overloading of 20%). Beside several leakages in primary pipelines ($\varnothing 16$ mm), which can be in case of VVER-440 SGs relatively easy solved (blended), the corrosion deposits in feed water pipeline system occurred at many VVER-440 units [9]. The identified damages were caused mostly due to corrosion/erosion processes attacking materials familiarly called "black steels" with insufficient resistance against corrosion.

Based on experience from Finland, also other countries including Slovakia changed the old feed water pipeline system. At this moment we would like to mention that the incident at the 2nd unit of NPP Paks (Hungary, 2003) connected to cleaning of fuel assemblies in special tank had the root causes in insufficient passivation of pipelines in SG after the steam water pipeline system exchange in 1997.

All steam generators at four VVER-440 units in Bohunice were gradually changed. At that time, there were two possibilities for the new feed water pipeline system. Out from two conceptions: Vítkovice a.s. design and OKB Hidropress design. The first solution was selected and lately improved to so called "Bohunice solution". Actually, experience from the last 10 years after upgrade was utilized.

A detailed description of VVER-440 steam generators delivered to NPP Bohunice is in [10-12]. The safety analyses were performed in 1977 by OKB Hidropress according to the Russian norms. The Russian designer and producer made the feed water pipelines (secondary side) from the carbon steel (GOST norm 20K and 22K). Water inlet pipeline was connected to the T-junction. From this point, 2 lines of the pipe with nozzles distributed the cooling secondary water in the space between primary pipes. Several problems having occurred in other NPPs were published in [13-16]. A disadvantage of such steam generators are difficult accessibility to the T-junction and next pipelines in the bundle.

3.1 Design changes at VVER-440 steam generators

The steam generator with technical mark RGV-4E is one body SG [10-12]. The heat-exchange area is incorporated inside as surface of primary pipelines bundle with U-shape. The ends of these pipelines are fixed to the walls of the primary collector. Inside of SG body several separators and system of the steam water distribution are placed. The PGV-4E steam generator is foreseen for dry steam production with the pressure of about 4,61 MPa at a temperature of about 258°C.

The basic 1977 design from was improved after 1994 by new feed water pipeline system. There was also change in the type of steel of these pipelines. Instead conventional carbon steel, the austenite steel was used in distribution boxes as well as feed water pipelines.

All components in the Bohunice innovated feed water pipeline system were made of austenitic steel according to the Czechoslovak norm ČSN, class 17. Advantages of the new construction are not only higher resistance against corrosion, but also much more comfortable visual inspection. The innovations can be seen in Figs. 1, 2.

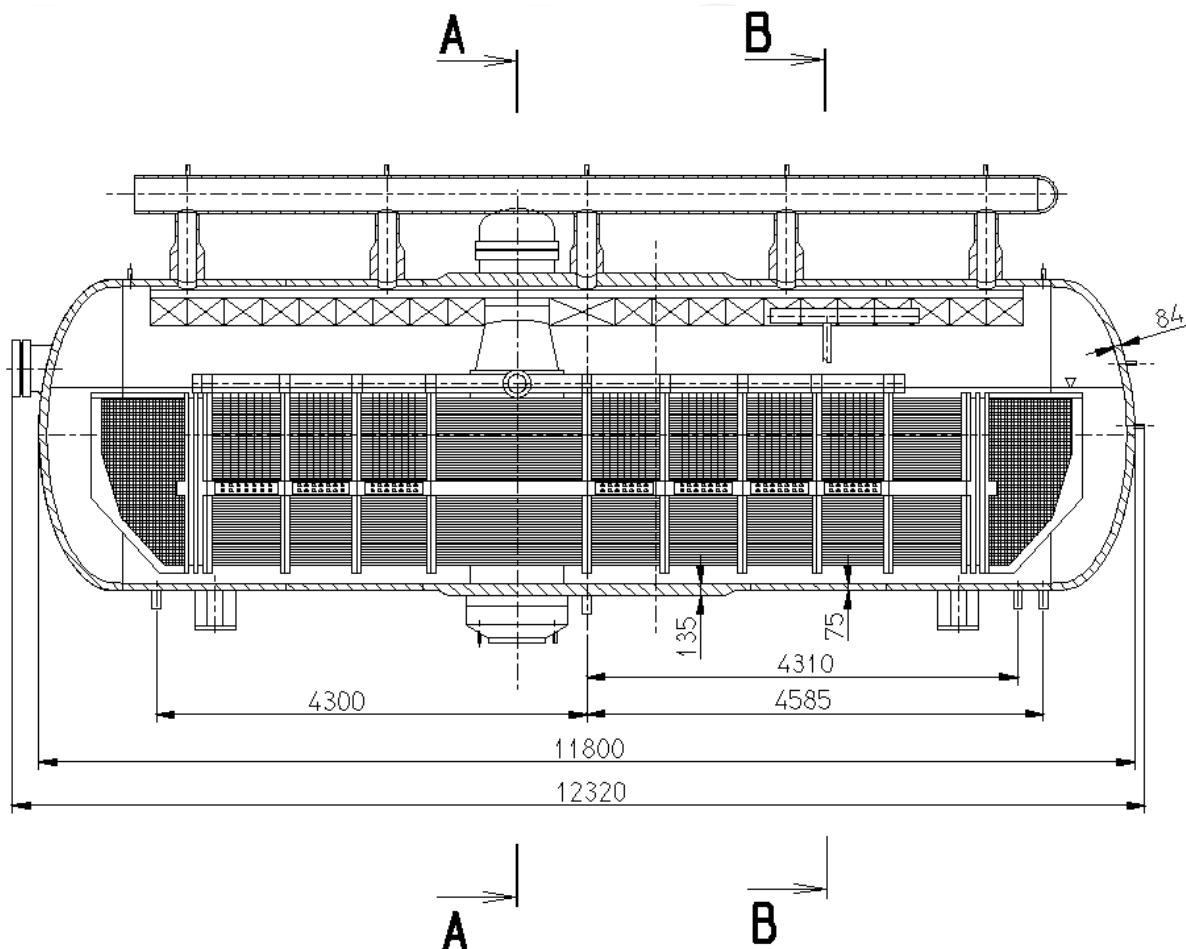


Fig. 1. VVER-440 (Bohunice) steam generator - cross section. NPP Bohunice innovation

The feed water comes via nozzle to distribution pipeline system and gets inside to left and right incoming line. From this place, water flows via pipelines $\phi 44,5 \times 4$ mm into chambers and gets out via ejectors. This flow is mixed together with boiler water, so the final flow on the small primary pipelines is not extremely hot and does not cause a disturbing thermal load. Simultaneously, the circulation in SG tank was improved and places with increased salt concentration are reduced.

The main advantage is that the visual inspection of the feed water pipeline can be performed immediately due to placement of the whole water distribution system over the primary pipelines bundle. Using this system, the possible defects are easier observable. The next advantage is connected to 7 boxes with ejectors which mix properly the feed water with boiler water and the thermal load decreases in this way. An additional advantage is the checking and exchange possibility of distribution boxes in case of their damage.

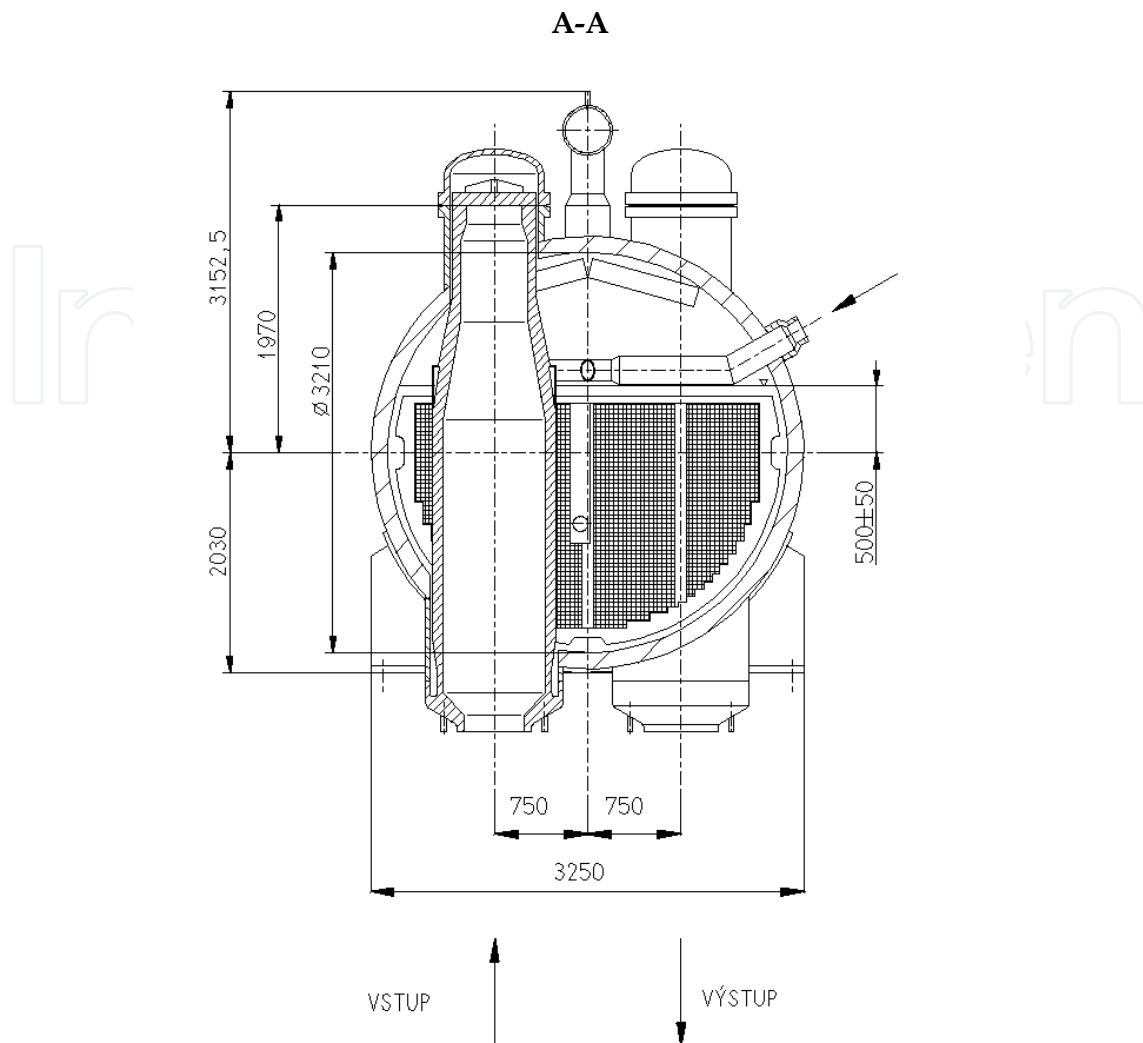


Fig. 2. VVER-440 (Bohunice) steam generator – cross section A-A, NPP Bohunice innovation

4. Experimental

For the experimental measurements, several specimens containing corrosion products were taken from different parts of all of 4 NPP Bohunice units. In the first step, corrosion process at the steam generators was studied. The corrosion layers were separated by scraping the rust off the surface and the powder samples were studied by transmission Mössbauer spectroscopy. It should be noted that the gamma spectroscopic measurements gave no evidence of the presence of low-energy gamma radiation emitted from the samples. Later, the corrosion products were collected also from different parts of secondary circuit components and several filter deposits were analysed as well.

The room temperature Mössbauer study was performed on two different steam generator materials using conventional transmission Mössbauer spectrometer with the source ^{57}Co in Rh matrix. The spectra were fitted using NORMOS program.

The original STN 12022 material used at the 4th (SG46) over 13 years was compared to STN 17247 steel used at the 3rd unit (SG35) for about 5 years (1994-1998). The chemical compositions of both materials are shown in Table 1.

Steam-generator	Type of the steel	Chemical composition [weight %]							
		C	Mn	Si	Cr	Ni	Ti	P	Cu
SG35	STN 17247	max. 0,08	max. 0,08	max. 1,0	17,0 - 19,0	9,5 - 12,0	Min. 5x%C	max. 0,045	-
SG46	STN 12022 (GOST 20K)	0,16- 0,24	0,35- 0,65	0,15-0,30	max. 0,25	max. 0,25	-	0,04	Max. 0,3

Table 1. Chemical composition of investigated base material

Samples of corrosion products scrapped from different parts of the steam generators SG 35 and SG46 were analysed. The scrapped corrosion particles were homogenised by granulation and sieved through a of 50µm wire sieve.

5. Results from Mössbauer spectroscopy analyses

The advanced evaluation of phase analyses of corrosion products from different parts of VVER-440 steam generators via Mössbauer spectroscopy is our active and unique contribution in this area. The scientific works go over 25 years. The first period (mostly 80-ties) was important for improving Mössbauer technique. The benefit from this period is mostly in experience collection, optimization of measurement condition and evaluation programs improvement [5]. Unfortunately, not all specimens were well defined. Having in mind also different level of technique and evaluation procedures, it would be not serious to compare results from that period with the results obtained from measurement after 1998.

5.1 Comparison of the corrosion products before and after SG design changes

In the period 1994-1999 we focused our study on the comparison of the phase composition of corrosion products taken from the NPP Bohunice before and after changes in the feed water pipeline system.

Schematic drawings of VVER steam generators (SG) with indicated places of scrapped corrosion specimens are presented in Fig.3.

Serious damages were observed in the region of T-junction (position 4 in Fig.3) as well as of pipe-collector and outlet nozzles on many VVER440 SGs after approximately ten years of operation [9,17]. Therefore, the former feed-water distributing system has been replaced by an advanced feed-water distributing system of EBO design at SGs of NPP Jaslovske Bohunice [18, 19]. The advanced system consists of a V-shaped junction connected to the left - and the right part water distributing chambers both located above the tube bundle and few feed water boxes with water ejectors inserted into the tube bundle and connected to the distributing chamber by distributing pipelines.

After five year's operation in the SG No. 35 in the NPP outage one feed water box and corresponding distributing pipelines were replaced by new ones with the aim to analyse their overall stage and corrosion products on walls. For comparison, some parts of the former feed-water-distributing system from the SG Number 46 were cut out and analysed.

More than 50 specimens were collected from the NPP Bohunice secondary circuit in 1998-2000. The investigation was focused mainly on the corrosion process going on in steam

generators SG35 with new design and SG46 with old design. Nevertheless, additional measurements performed on the corrosion products from SG31 and SG32 confirmed that corrosion process in all 6 steam generators of one reactor unit is the same and corrosion layers are on the some places altogether identical.

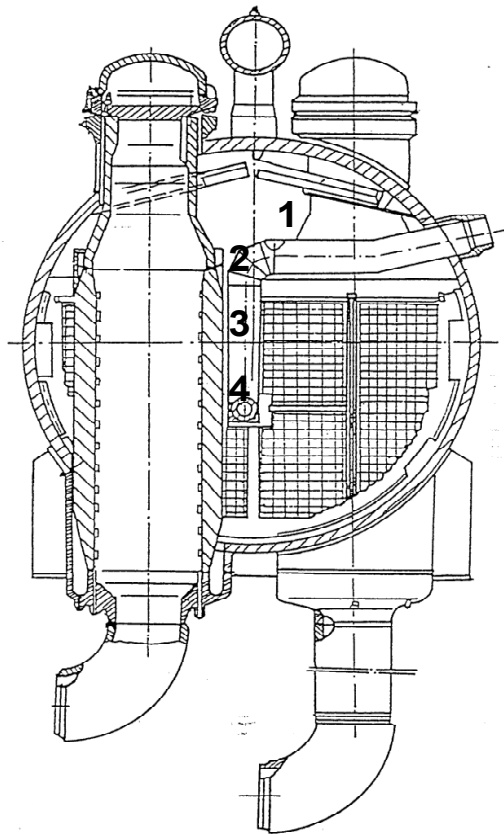


Fig. 3. Cross section of SG46 (Numbers indicate the places, where the specimens were scrapped)

All measured specimens contain iron in magnetic and many times also in paramagnetic phases. Magnetic phases consist in form of nearly stoichiometric magnetite ($\gamma\text{-Fe}_3\text{O}_4$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), and in some case also iron carbides. The paramagnetic fractions are presented in Mössbauer spectra by a doublet and a singlet. Its parameters are close to hydro-oxide (FeOOH) parameters or to parameters of small, so called superparamagnetic particles of iron oxides (hydroxides) with the mean diameter of about 10 nm (see Table 2 and Table 3).

MS confirmed its excellent ability to identify steel samples phase composition although its sawdust form and relative small amount (~ 100 mg). Our experiences with such measurements applied on different VVER-440 construction materials were published in [15, 20-21]. From other works it is possible to mention [22]. MS confirmed an austenitic structure of STN 17247 steel and ferrite structure of STN 12022 steel. Differences between these two materials are well observable (see Table 2 and Fig. 4 and Fig. 5). According to the *in-situ* visual inspections performed at SG35 (1998) and SG46 (1999) as well as MS results, significant differences in corrosion layers and material quality were observed. The feed water tubes in SG46 were significantly corroded after 13 years operation.

Sample	Sextets						Singlet		
	H ₁	A _{rel}	H ₂	A _{rel}	H ₃	A _{rel}	IS	A _{rel}	Fig.
(sawdust)	(T)	(%)	(T)	(%)	(T)	(%)	(mm/s)	(%)	
SG35	29.3	18.7	26.3	18.5	22.8	27.4	-0.12	35.4	4
SG46	33.3	80.5	31.2	19.5		-	-	-	5
Accuracy	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5	±0,04	±0,04	

Table 2. MS parameters of the steam generators base material

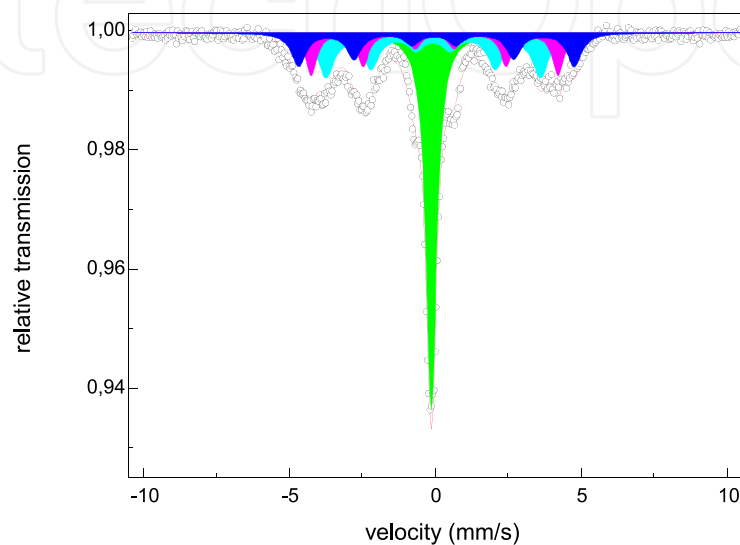


Fig. 4. MS spectrum of SG35 base material

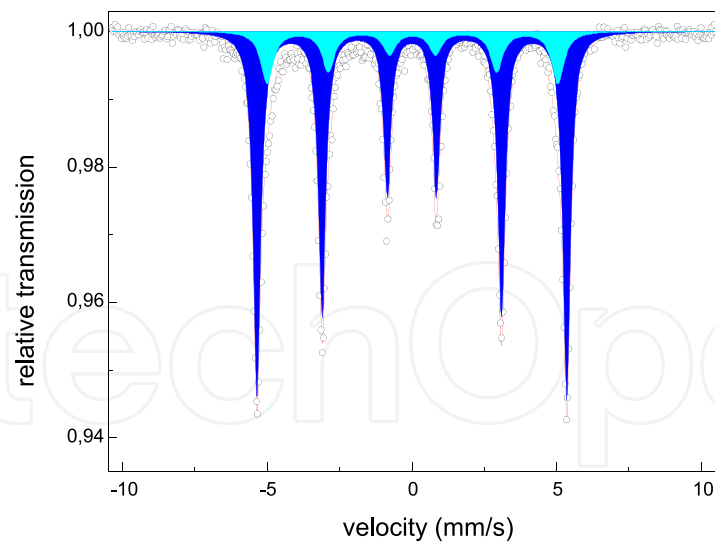


Fig. 5. MS spectrum of SG46 base material

Our results confirmed that during operation time a faint oxidation surroundings was in the observed steam generator SG35 after 5 years of operation time and the corrosion samples were fully without base material particles.

Magnetite was identified as dominant component in all studied samples (see Table 3). Mössbauer spectrum of the steam generators (both SG35 and SG46) surface layer is the

superposition of two sextets with hyperfine magnetic field $H_{\text{efA}} = 49,4\text{T}$ and $H_{\text{efB}} = 45,8\text{T}$. Sextet H_{efA} corresponds to the Fe^{3+} ions in tetrahedral (A) sites and sextet H_{efB} corresponds to Fe^{2+} and Fe^{3+} ions in octahedral (B) sites in magnetite spinel structure (Fe_3O_4).

Sample	Magnetite					Doublet			Singlet	
	H_A (T)	A_{rel} (%)	H_B (T)	A_{rel} (%)	r_{AB} (a.u.)	IS (mm/s)	QS (mm/s)	A_{rel} (%)	IS (mm/s)	A_{rel} (%)
L754	49.0	35.0	45.9	65.0	0.538					
L755	49.0	35.3	45.9	64.7	0.546					
L757	49.0	34.8	45.9	65.2	0.534					
L758	49.0	34.1	45.9	62.3	0.547				-0.20	3.6
L789	49.0	34.4	46.0	65.6	0.535					
L790	49.0	34.9	46.0	64.3	0.543				-0.18	0.8
L759	49.0	35.4	45.9	63.9	0.534				-0.20	0.7
L777	49.0	35.0	45.9	65.0	0.538					
L786	49.0	35.2	46.0	64.8	0.545					
L787	49.1	36.5	46.0	56.1	0.651	0.22	0.67	2.0	-0.20	5.4
L760	49.0	34.1	45.9	64.3	0.530				-0.17	1.6
L761	49.0	35.0	45.9	63.9	0.547				-0.23	1.1
L762	49.1	34.8	46.0	56.4	0.617				-0.20	8.8
L779	49.0	33.4	45.9	62.9	0.531				0.10	3.7
Accuracy	$\pm 0,1$	$\pm 0,5$	$\pm 0,1$	$\pm 0,5$		$\pm 0,04$	$\pm 0,04$	$\pm 0,5$	$\pm 0,04$	$\pm 0,5$

Table 3. MS parameters of corrosion products taken from the steam generator SG35¹

In contrast to magnetite, whose spectrum is characterised by two sextets, the hematite phase present in the powders gives a single sextet. The relatively narrow line width (Γ) of the α - Fe_2O_3 (mainly $0,24 \div 0,26$ mm/s) indicates presence of a well-crystallised phase with few, if any, substitutions of other elements for Fe. However, in some spectra (mainly from filter deposits studied later), both the lower hyperfine field and the larger width (about $0,33 - 0,34$ mm/s) could indicate a poorer crystallinity and/or a higher degree of substitution. These findings are in good agreement with those obtained by E. De Grave [23]. Similar inspirational results (focused also on corrosion products from VVER-440 construction materials) were published in [24-26].

For the ideal stoichiometric Fe_3O_4 the quantity r_{AB} (ratio between A and B sub-component areas) is equal to 0.535. In the case that magnetite is the dominant (sole) phase in the sample, the deviation from the ideal value of r_{AB} is minimal (see Table 3). Significant deviations could be explained by a small degree of oxidation of magnetite, resulting in presence of vacancies or substitution by non/magnetic irons in the octahedral sub-lattice. Slight substitution of other elements (Mg, Ni, Cu, ...) for Fe in the magnetite lattice is not unlikely, and this has a similar effect on the A- to B-site area ratio. Therefore, it is not feasible to conclude anything quantitatively about the degree of oxidation. Qualitatively, it can be inferred that this degree must be very low.

¹ Samples L754-L757 were taken from the feed water pipelines *in situ* during the reactor shut down. Samples L758-L790 were taken from the same steam generator from selected parts of feed water dispersion box (see Table 3 and Fig. 6, positions 1-14)

During visual inspection of removed feed water dispersion box (1998), 2 disturbing undefined metallic particles, fixed in one of outlet nozzle, were found. Both were homogenised and analysed by MS. It has been shown that these high-corroded parts ("loose parts" found in outlet nozzle of ejector) originate not from the 17247 steel but high probably from GOST 20K steel (probably some particles from the corrosion deposit from the bottom part of the steam generator moved by flow and ejection effect into the nozzle).

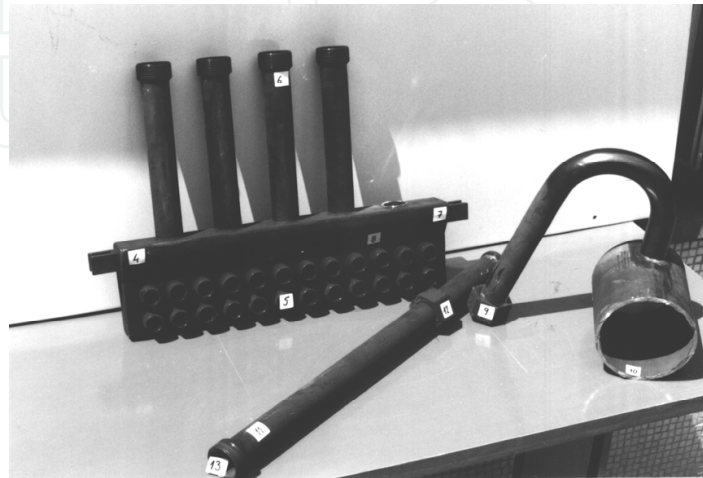


Fig. 6. Position of corrosion product scraps from the feed water dispersion box (SG35)

Code	Hematite		Magnetite				Base material				Doublet 1		Doublet 2	
	H1	A _{rel}	H _A	A _{rel}	H _B	A _{rel}	H4	A _{rel}	H5	A _{rel}	IS1	A _{rel}	IS2	A _{rel}
	(T)	%	(T)	%	(T)	%	(T)	%	(T)	%	(mm/s)	%	(mm/s)	%
M005			49.0	35.4	45.8	64.6								
M006			49.1	36.5	45.9	63.5								
M007	50.0	16.9	49.2	25.6	45.8	38.2	33.0	1.6					0.84	17.7
M008			49.0	35.6	45.9	64.1								
M009	51.5	13.4	49.1	32.1	45.9	54.5								
M010			49.1	36.5	45.8	63.5								
M012	51.5	12.5	49.2	31.9	46.0	55.6								
M013			48.8	25.3	45.7	40.5	33.0	30.2	30.8	4.0				
M014			49.0	9.9	45.8	13.6	33.0	66.6	30.7	9.9				
M015			48.5	6.0	45.6	8.6	33.0	73.1	30.6	12.3				
Accuracy	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5	±0,1	±0,5

Table 4. MS parameters of corrosion products taken from the steam generator SG46²

² Samples m006, m008, m010 were taken from outside surface, samples M007, M009, M012 from inside surface of the feed water pipeline according to the same positions 1, 2 and 3, respectively. Sample M15 - see Fig. 7, position 7).

Mössbauer measurements on the corrosion specimens scrapped from different position of the feed water distributing system show that the outside layer consists exclusively from magnetite but the inside layer contains also hematite. Its amount decreases in successive steps towards the steam generator. The cause of this result is probably in fact that outside the system there is boiling water at the temperature of approximately 260 °C with higher salt concentrations and inside there is the feed water at the temperature up to 225 °C. Changes in the inside temperature in region (158-225 °C) can occur in dependence on the operation regime of high-pressure pumps in NPP secondary circuit.

The most corroded areas of the former feed water distributing system are the welds in the T-junction (see Fig. 7). Due to dynamic effects of the feed water flow with local dynamic overpressures of 20 to 30 kPa or local dynamic forces up to 1000 N (in the water at the pressure of about 4,4 MPa) on the inner pipe wall in the region of T-junction, the content of corrosion products was reduced and moved into whole secondary circuit. Particles of the feed water tube of SG46 base material were identified also in sediments.

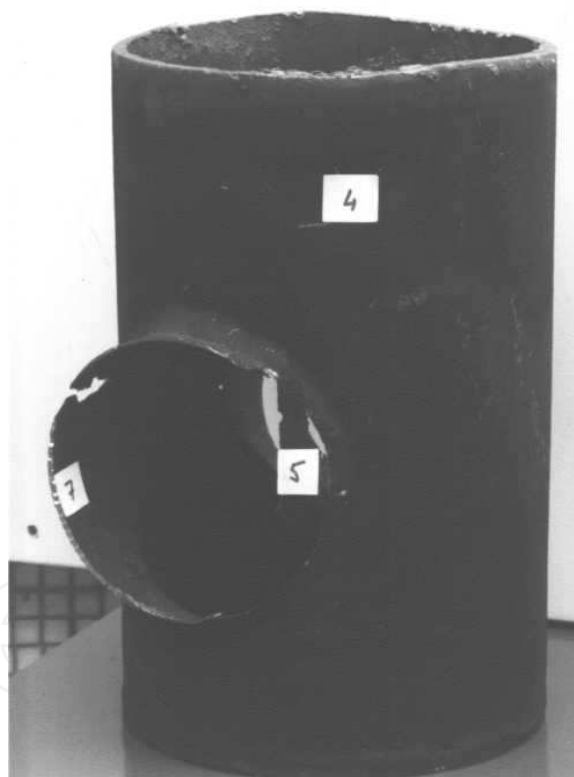


Fig. 7. Position of corrosion product scraps from the feed water dispersion tube (SG46)

5.2 Results from visual inspection of heterogenic weld at SG16 from April 2002

In the period 2002-2003 we focused on the „Phase analyses of corrosion induced damage of feed water pipelines of SG 16 near the heterogenic weld“. In frame of this study visual inspections as well as original “in situ” specimens scrapping was performed. Conclusions from visual inspections (performed at 19.4.2002 and 29.4.2002 at SG16) were the following:

SG16 was dried under the level of primary pipelines bundle and decontaminated. During the visual inspection of SG16 internal surface as well as hot and cold collectors (after 23 years of operation) no defects or cracks were identified. The SG16 was in excellent status with minimal thickness of corrosion layer or other deposits. For comparison to our previous experience from visual inspections from 1998, the SG16 was in better condition than SG35 or SG46 (14 and 13 years in operation, respectively). Moreover, the radiation situation after decommissioning procedures was two times better.

Visual inspection on 29.4.2002 was focused on heterogenic weld, which connects the feed water pipeline of carbon steel (GOST 20K) to a new feed water pipeline system designed from austenitic steel (CSN17248). Several samples were taken for MS analyse from the weld as well as surrounding area in form of powder or small particles (samples description is in Table 5 and in Figs 8, 9). The heterogenic weld was well polished.

After visual inspection, the evaluation of corrosion phase composition of samples closed to heterogenic weld was performed. MS results are summarized in Table 6.

Number of samples	Samples description
2.11	Heterogenic weld
2.12	Feed water pipeline (GOST 20), 10 cm from heterogenic weld
2.13	Feed water pipeline (GOST 20), about 40 cm from heterogenic weld, just closed to the SG16 internal body surface.
2.14	Internal body surface, about 1 m under the place of feed water pipeline inlet
2.15	Internal body surface, about 50 cm over the place of feed water pipeline inlet

Table 5. Specimens description

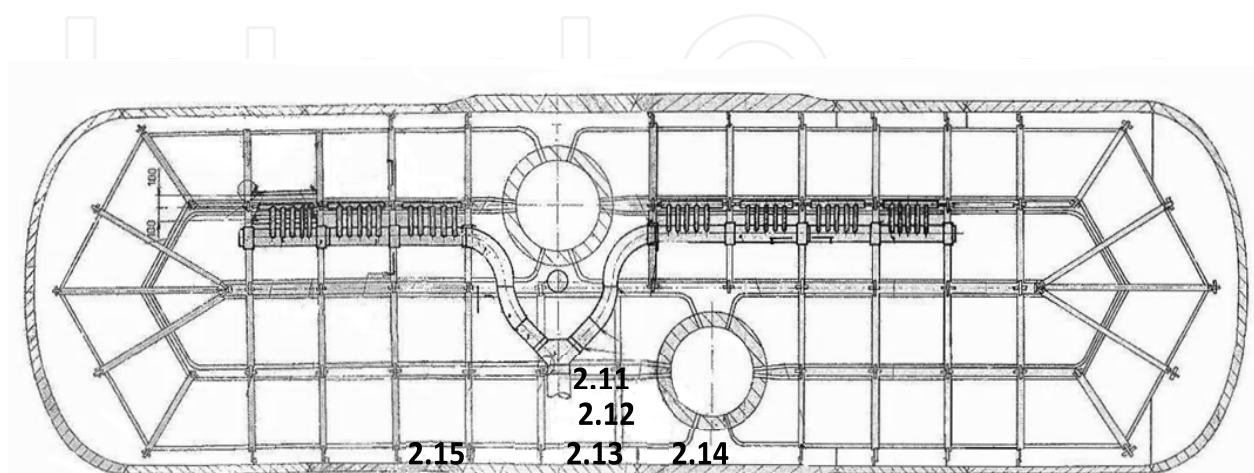


Fig. 8. SG16 with marks and description of places, where MS specimens were taken

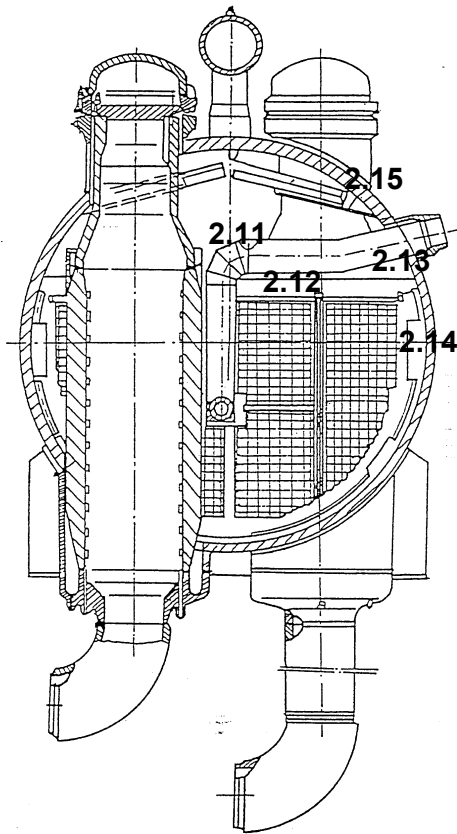


Fig. 9. SG16 cross section with indicated places where specimens were taken

Sample	Haematit				Magnetite						Mag. total	Metalic iron			Dublet/singlet		
	H ₁	QS ₁	IS ₁	A _{rel1}	H ₂	IS ₂	A _{rel2}	H ₃	IS ₃	A _{rel3}		H ₄	IS ₄	A _{rel4}	QS ₄	IS ₄	A _{rel4}
	(T)	(mm/s)	(mm/s)	(%)	(T)	(mm/s)	(%)	(T)	(mm/s)	(%)		(T)	(mm/s)	(%)	(mm/s)	(mm/s)	(%)
2.11	51,9	-0,18	0,25	8,0	49,0	0,17	3,8	45,9	0,57	8,0	11,8	33,0	-0,11	12,8	-	-0,19	67,4
2.12	51,6	-0,21	0,26	75,9	49,0	0,16	9,1	45,8	0,56	14,1	23,2	-	-	-	0,40	0,21	0,9
2.13	51,6	-0,21	0,26	77,2	49,0	0,17	9,2	45,9	0,57	12,9	22,1	-	-	-	0,40	0,21	0,7
2.14	51,6	-0,21	0,26	41,1	49,0	0,16	22,0	45,8	0,55	36,9	58,9	-	-	-	-	-	-
2.15	51,8	-0,21	0,26	51,7	49,1	0,17	18,3	45,9	0,54	29,2	47,5	-	-	-	0,40	0,21	0,8
Accuracy	±0,1	±0,04	±0,04	±2	±0,1	±0,04	±0,1	±0,1	±0,04	±2	±2	±0,1	±0,04	±2	±0,04	±0,04	±2

Table 6. Mössbauer spectra parameters

Sample	Hematite				Magnetite							Dublet			
	H ₁	QS ₁	IS ₁	A _{rel1}	H ₂	IS ₂	A _{rel2}	H ₃	IS ₃	A _{rel3}	Spolu	QS ₁	IS ₁	A _{rel1}	
	(T)	(mm/s)	(mm/s)	(%)	(T)	(mm/s)	(%)	(T)	(mm/s)	(%)	(%)	(mm/s)	(mm/s)	(%)	
2.16	51.6	-0.21	0.26	66.4	49.1	0.17	12.1	45.9	0.56	19.6	31.7	0.53	0.23	1.9	
2.17	51.6	-0.21	0.26	80.8	49.1	0.16	6.6	46.0	0.55	11.5	18.1	0.47	0.21	1.1	
2.18	51.6	-0.21	0.26	33.4	49.0	0.16	22.6	45.9	0.55	42.9	65.5	0.52	0.09	1.1	
2.19	51.6	-0.21	0.26	40.3	49.0	0.16	20.5	45.9	0.56	38.0	58.5	0.52	0.13	1.2	

Table 8. MS results of specimens taken in 2004 in Bohunice V1 from SG11.

5.3 Results from SG11 (2004)

Four powder specimens were delivered from SG11 to MS analyses. Description is shown in Table 7 and results in Table 8.

Sample	Description of origin	Date of extraction
2.16	Hot collector, HC-SG-11	15.03.04 9:00 h.
2.17	Cold collector, SC-SG-11.	15.03.04 9:00 h.
2.18	SG11 sediments	16. 03.04 10:00 h.
2.19	SG11 sediments cooler (surface of pipelines)	16. 03.04 10:00 h.

Table 7. Specimens from SG11 analysed in 2004

The dominant phase composition of the studied corrosion products taken from SG11 was hematite Fe_2O_3 (66,4% at hot collector, 80,8% at cold collector). The rest is from magnetite Fe_3O_4 , presented by two sextets H_2 and H_3 with 31,7%, resp.18,1% contribution. The last component is paramagnetic doublet D_1 , which is assumed to be iron hydroxides - high probably lepidocrocite ($\gamma\text{-FeOOH}$) presented by 1,9% and 1,1%, respectively.

The magnetite presence in all samples is almost stoichiometric (see the ratio $\text{Fe}^{3+}/\text{Fe}^{2+}$ which tends to 2,0).

A significantly lower presence of magnetite in case of hot collector can be devoted from 2 parallel factors:

1. Difference in temperature (about 298°C at HC) and (about 223°C at CC) and mostly due to
2. Higher dynamic of secondary water flowing in the vicinity of hot collector, which high probably removed the corrosion layer from the collector surface.

5.4 Period 2006-2008 – The newest measurement of corrosion products at NPP Jaslovske Bohunice

Six samples for Mössbauer effect experiments collected from different parts of NPP Bohunice unit were prepared by crushing to powder pieces (Table 9). These samples consisted of corrosion products taken from small coolant circuit of pumps (sample No. 3.1), deposits scraped from filters after filtration of SG - feed water during operation (sample No. 3.2), corrosion products taken from SG42 pipelines - low level (sample No. 3.3), mixture of corrosion products, ionex, sand taken from filter of condenser to TG 42 (sample No. 3.4), deposit from filters after refiltering 340 l of feed water of SG S3-09 during passivation 27. and 28. 5. 08 (sample No. 3.5) and finally deposit from filters after 367 l of feed water of SG S4-09 during passivation 27. and 28. 5. 08 (sample No. 3.6). All samples were measured at room temperature in transmission geometry using a $^{57}\text{Co}(\text{Rh})$ source. Calibration was performed with $\alpha\text{-Fe}$. Hyperfine parameters of the spectra including spectral area (A_{rel}), isomer shift (IS), quadrupole splitting (QS), as well as hyperfine magnetic field (B_{hf}), were refined using the CONFIT fitting software [27], the accuracy in their determination are of $\pm 0.5\%$ for relative area A_{rel} , ± 0.04 mm/s for Isomer Shift and Quadrupole splitting and ± 0.5 T for hyperfine field correspondingly. Hyperfine parameters of identified components (hematite, magnetite, goethite, lepidocrocite, feroxyhyte) were taken from [28].

All measured spectra contained iron in magnetic and many times also in paramagnetic phases. Magnetic phases contained iron in nonstoichiometric magnetite $\text{Fe}_{3-x}\text{M}_x\text{O}_4$ where M_x are impurities and vacancies which substitute iron in octahedral (B) sites. Another magnetic fraction is hematite, $\alpha\text{-Fe}_2\text{O}_3$. In one sample also the magnetic hydroxide (goethite $\alpha\text{-FeOOH}$) was identified.

Paramagnetic fractions are presented in the spectra by quadrupole doublets (QS). Their parameters are close to those of hydroxides e.g. lepidocrocite $\gamma\text{-FeOOH}$ or to small, so called superparamagnetic particles of iron oxides or hydroxides with the mean diameter of about 10 nm. It should be noted that there is no problem to distinguish among different magnetically ordered phases when they are present in a well crystalline form with low degree (or without) substitution. Both the substitutions and the presence of small superparamagnetic particles make the situation more complicated [29]. In such cases, it is necessary to perform other supplementary measurements at different temperatures down to liquid nitrogen or liquid helium temperatures without and with external magnetic field [30].

Mössbauer spectrum (Fig. 10) of sample no. 3.1 (corrosion products taken from small coolant circuit of pumps) consist of three magnetically split components, where the component with hyperfine field $B_{\text{hf}} = 35.8$ T was identified as goethite ($\alpha\text{-FeOOH}$). Hyperfine parameters of remaining two magnetically split components are assigned to A - sites and B - sites of magnetite (Fe_3O_4). One paramagnetic spectral component has appeared. According to water environment and pH [31], this component should be assigned to hydroxide (feroxyhyte $\delta\text{-FeOOH}$).

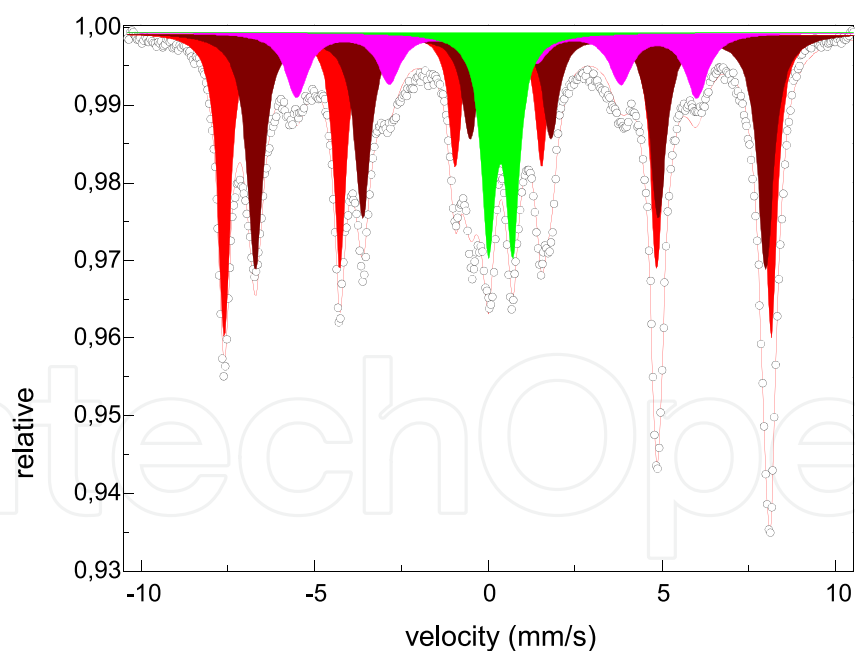


Fig. 10. Mössbauer spectrum of sample no. 3.1. A-site (red), B-site (dark red) magnetite, goethite (pink) and hydroxide (green) was identified

The sample No. 3.2 (deposits scraped from filters after filtration of SG - feed water during operation) also consists of three magnetically split components, where two of them were assigned to magnetite (Fe_3O_4) as in previous spectra, and the remaining magnetically split component was identified as hematite ($\alpha\text{-Fe}_2\text{O}_3$). Paramagnetic part of the spectra was

formed by one doublet, whose hyperfine parameters were assigned to hydroxide (lepidocrocite, γ -FeOOH). The spectrum is shown in Fig. 11.

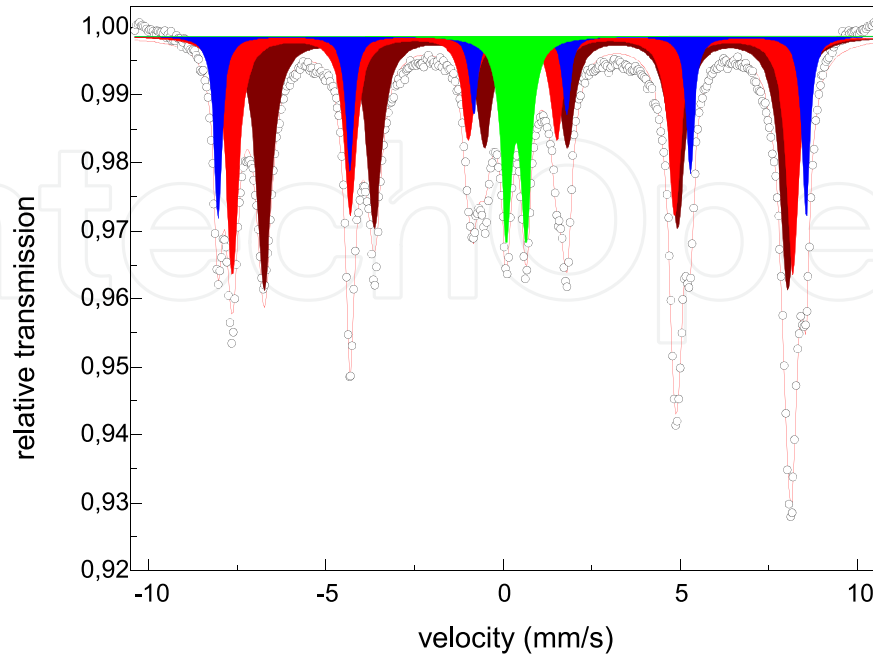


Fig. 11. Mössbauer spectrum of sample no.3. 2. A-site (red), B-site (dark red) magnetite, hematite (blue) and hydroxide (green) was identified

The spectrum (Fig. 12) of the sample No. 3.3 (corrosion products taken from SG42 pipelines - low level) consists only of two magnetically split components with hyperfine parameters assigned to A - sites and B - sites of nearly stoichiometric magnetite (Fe_3O_4) with a relative area ratio $\beta = 1.85$.

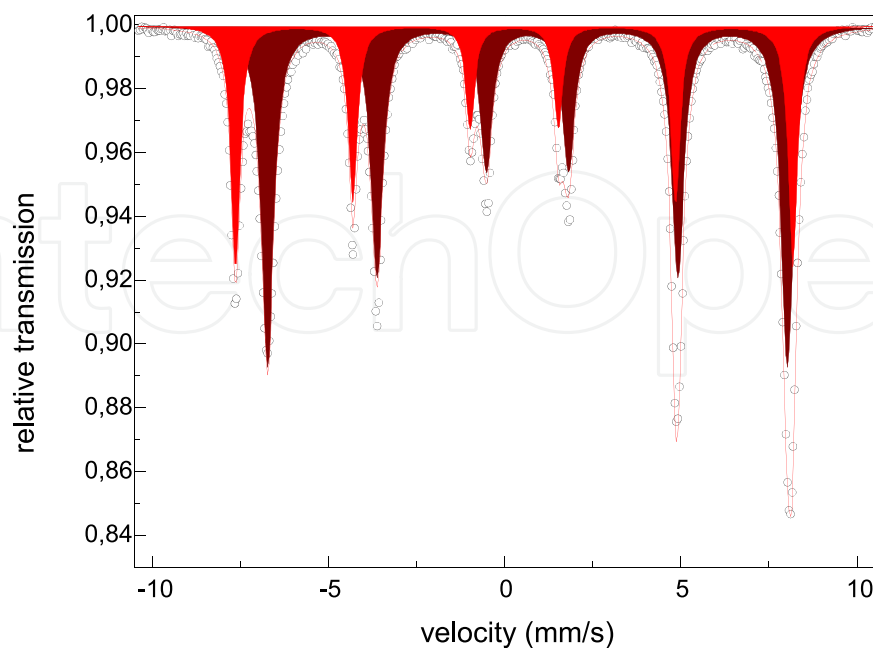


Fig. 12. Mössbauer spectrum of sample no. 3.3. A-site (red) , B-site (dark red) magnetite was identified

The sample No. 3.4 (mixture of corrosion products, ionex, sand taken from filter of condenser to TG 42) also consists of a magnetically split component which corresponds to hematite ($\alpha\text{-Fe}_2\text{O}_3$) and two magnetically split components were assigned to magnetite (Fe_3O_4) as in previous spectra, and the remaining paramagnetic component was identified as hydroxide. The spectrum of the sample No. 3.4 is shown in Fig. 13.

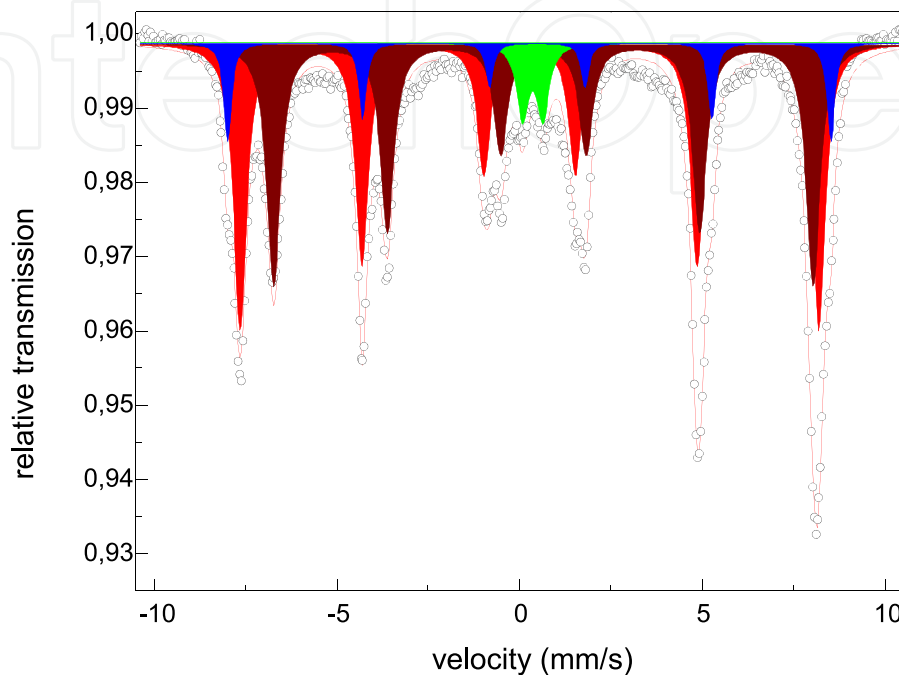


Fig. 13. Mössbauer spectrum of sample no. 3.4. Haematite (blue), A-site (red), B-site (dark red) magnetite and hydroxide (green) was identified

Both the sample No. 3.5 (deposit from filters after 340 l of feed water of SG S3-09 during passivation 27. and 28. 5. 08) and the sample No. 3.6 (deposit from filters after 367 l of feed water of SG S4-09 during passivation 27. and 28. 5. 08) consist of three magnetically split components, identified as hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) and the remaining paramagnetic component in both spectra was assigned to hydroxide (lepidocrocite $\gamma\text{-FeOOH}$). The spectra of the samples No. 3.5 and 3.6 are shown in Figs. 14 and 15. Based on comparison of results from samples 3.5 and 3.6 it can be concluded that the longer passivation leads more to magnetite fraction (from 88% to 91%) in the corrosion products composition.

As it was mentioned, above all hydroxides could be also small superparamagnetic particles.

The refined spectral parameters of individual components including spectral area (A_{rel}), isomer shift (IS), quadrupole splitting (QS), as well as hyperfine magnetic field (B_{hf}) are listed in Table 9 for room (300 K) temperature Mössbauer effect experiments. The hyperfine parameters for identified components (hematite, magnetite, goethite, lepidocrocite, feroxyhyte) are listed in [28].

Major fraction in all samples consists of magnetically ordered iron oxides, mainly magnetite (apart from the sample No. 3.1 and 3.2, where also goethite and hematite has appeared, respectively). Magnetite crystallizes in the cubic inverse spinel structure. The oxygen ions form

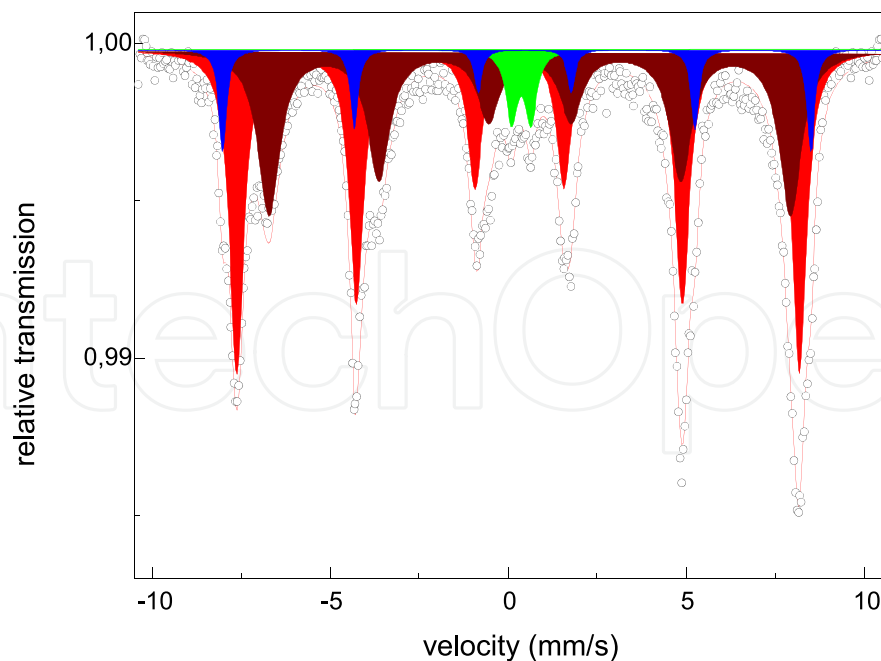


Fig. 14. Mössbauer spectrum of sample no.3.5. Hematite (blue), A-site (red), B-site (dark red) magnetite and hydroxide (green) was identified

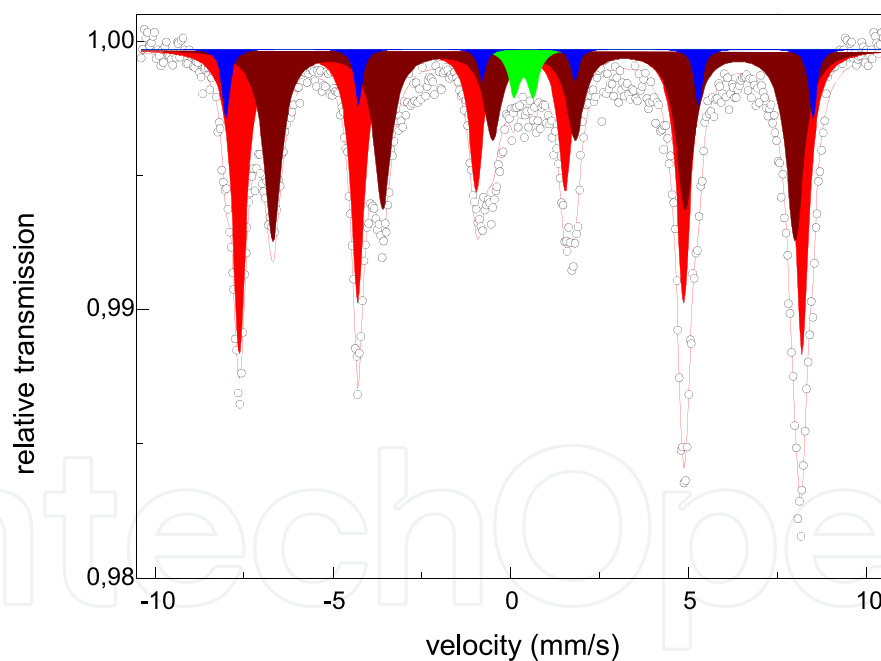


Fig. 15. Mössbauer spectrum of sample no. 3.6. Hematite (blue), A-site (red), B-site (dark red) magnetite and hydroxide (green) was identified

a closed packed cubic structure with Fe ions localized in two different sites, octahedral and tetrahedral. The tetrahedral sites (A) are occupied by trivalent Fe ions. Tri- and divalent Fe ions occupying the octahedral sites (B) are randomly arranged at room temperature because of electron hopping. At room temperature, when the electron hopping process is fast, the Mössbauer spectrum is characterized by two sextets. The one with the hyperfine magnetic field $B_{hf} = 48.8$ T and the isomer shift $IS = 0.27$ mm/s relative to α -Fe corresponds to the Fe^{3+}

sample	Component	Area [%]	Isomer shift [mm/s]	Quadrupole shift/splitting [mm/s]	Hyperfine field [T]
Sample no. 3.1 Small coolant circuit of pumps 17. 10. 2007	magnetite A-site	36.3	0.28	0.00	48.90
	magnetite B-site	37.2	0.64	0.00	45.60
	goethite	14.4	0.36	-0.25	35.80
	hydroxide	12.1	0.36	0.70	-
Sample no. 3.2. Deposites scraped from filters after filtration of SG - feed water during operation	hematite	15.8	0.38	-0.23	51.56
	magnetite A-site	32.6	0.28	0.00	49.14
	magnetite B-site	41.8	0.65	0.00	45.91
	hydroxide	9.7	0.38	0.56	-
Sample no. 3.3. SG42 pipelines - low level	magnetite A-site	34.6	0.28	0.00	49.14
	magnetite B-site	65.4	0.65	0.00	45.83
Sample no. 3.4. Mixture of corrosion products, ionex, sand taken from filter of condenser to TG 42	hematite	9.2	0.38	-0.22	51.29
	magnetite A-site	45.4	0.28	0.00	49.20
	magnetite B-site	40.7	0.66	0.00	45.87
	hydroxide	4.7	0.37	0.56	-
Sample no. 3.5. Deposit from filters after 340 l of feed water of SG S3-09 during pasivation 27. and 28. 5. 08	hematite	8.3	0.36	-0.22	51.33
	magnetite A-site	49.3	0.30	0.00	49.11
	magnetite B-site	38.5	0.61	0.00	45.51
	hydroxide	3.9	0.37	0.55	-
Sample no. 3.6. Deposit from filters after 367 l of feed water of SG S4-09 during pasivation 27. and 28. 5. 08	hematite	6.4	0.38	-0.25	51.26
	magnetite A-site	50.3	0.29	0.00	49.14
	magnetite B-site	40.7	0.66	0.00	45.61
	hydroxide	2.6	0.37	0.54	-

Table 9. Spectral parameters of individual components including spectral area (A_{rel}), isomer shift (IS), quadrupole splitting (QS), as well as hyperfine magnetic field (B_{hf}) for each sample with according components

ions at the tetrahedral A - sites. The second one with $B_{\text{hf}} = 45.7$ T and $IS = 0.65$ mm/s is the $\text{Fe}^{2.5+}$ - like average signal from the cations at octahedral B sites. Fe^{2+} and Fe^{3+} are indistinguishable due to fast electron transfer (electron hopping), which is faster (~ 1 ns) than the ^{57}Fe excited state lifetime (98 ns). The magnetite unit cell contains eight Fe^{3+} ions and eight Fe^{2+} and Fe^{3+} ions, 16 in total at the B sites, therefore, the intensity ratio $\beta = I(\text{B})/I(\text{A})$ of the two spectral components is a sensitive measure of the stoichiometry. Assuming that the room temperature ratio of the recoil-free fractions $f_{\text{B}}/f_{\text{A}}$ for the B and A sites is 0.97 [32], the intensity ratio β for a perfect stoichiometry should be 1.94. In non-stoichiometric magnetite, under an excess of oxygen, cation vacancies and substitutions at the B sites are created. The vacancies screen the charge transfer and isolate the hopping process. For each vacancy, five Fe^{3+} ions in octahedral sites become trapped. In the Mössbauer spectrum these trapped Fe^{3+} ions at the octahedral sites and Fe^{3+} ions at tetrahedral sites are indistinguishable without applying an external magnetic field. Therefore, in the spectrum of non-stoichiometric magnetite, intensity transfer from the $\text{Fe}^{2.5+}$ to Fe^{3+} -like components is observed. Therefore, the intensity ratio β decreases markedly with the oxidation process, until the stoichiometry reaches the $\gamma\text{-Fe}_2\text{O}_3$ phase. It should be noted that in our samples the intensity ratio β is far from 1.94 (for perfect stoichiometry), varies from 0.97 up to 1.85.

6. Conclusions

Material degradation and corrosion are serious risks for long-term and reliable operation of NPP. The paper summarises results of long-term measurements (1984-2008) of corrosion products phase composition using Mössbauer spectroscopy.

The first period (mostly results achieved in 80-ties) was important for improving proper Mössbauer technique [5]. The benefit from this period came via experience collection, optimization of measurement condition and evaluation programs improvement. Unfortunately, the samples were not well defined and having in mind also different level of technique and evaluation procedures, it would be not serious to compare results from this period to results obtained from measurement after 1998.

The replacement of STN 12022 steel (in Russian NPP marked as GOST 20K) used in the steam generator feed water systems is necessary and very important from the operational as well as nuclear safety point of view. Steel STN 17 247 proved 5 years in operation at SG35 seems to be optimal solution of this problem. Nevertheless, periodical inspection of the feed water tubes corrosion (after 10, 15 and 20 years) was recommended.

Based on results of visual inspection performed at April 19, 2002 at SG16 (NPP V1) it was confirmed, that the steam generator was in good condition also after 23 years of operation. Samples taken from the internal body surface of PG16 confirmed that the hematite concentration increases in the vertical direction (from bottom part to the top).

The newest results from 2008 confirm good operational experiences and suitable chemical regimes (reduction environment) which results mostly in creation of magnetite (on the level 70% or higher) and small portions of hematite, goethite or hydroxides.

Regular observation of corrosion/erosion processes is essential for keeping NPP operation on high safety level. The output from performed material analyses influences the optimisation of operating chemical regimes and it can be used in optimisation of regimes at

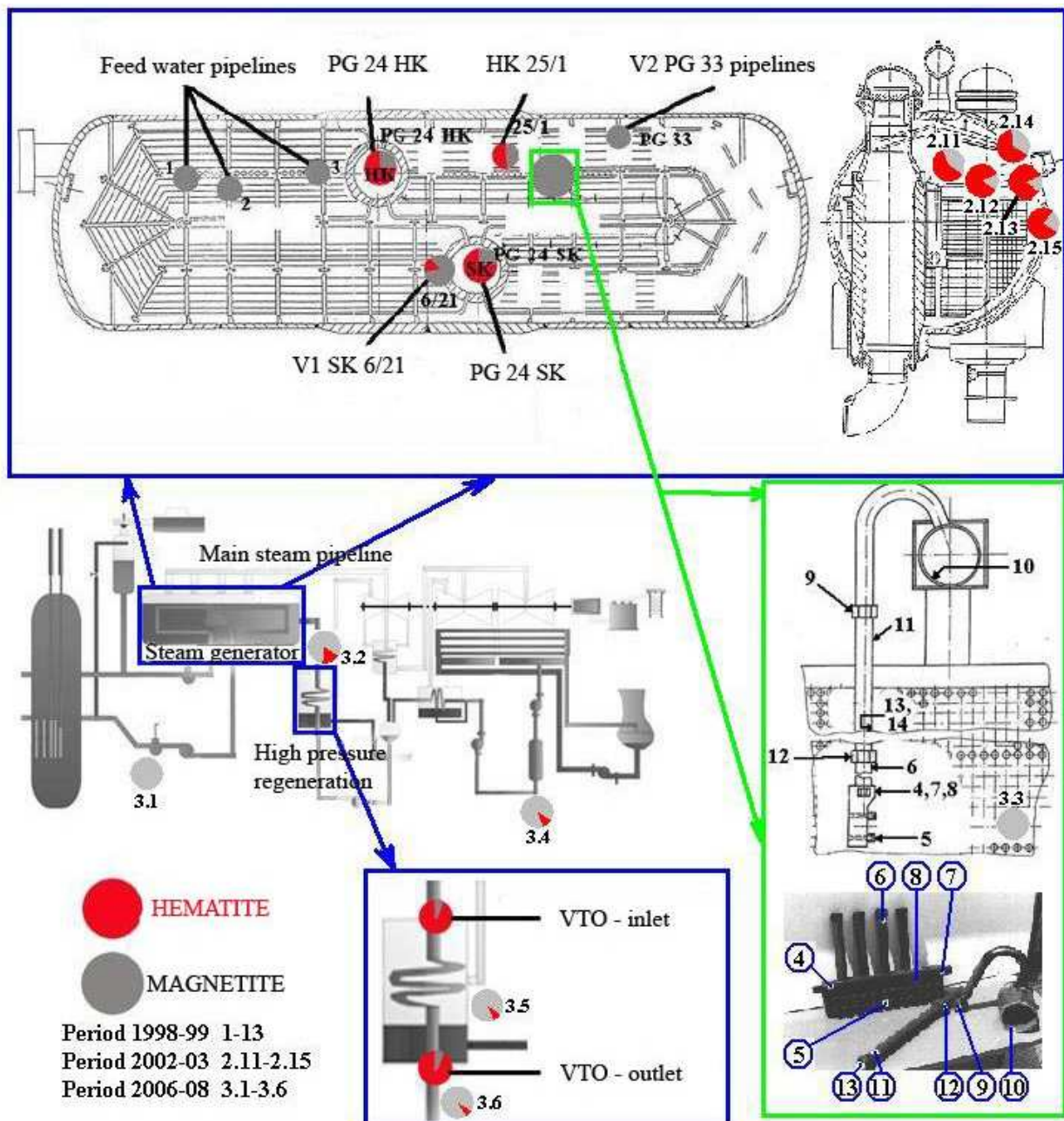


Fig. 16. Summarized figure of corrosion products phase composition at NPP V-2 Bohunice (Slovakia) performed according to results from period 1998-2008

decontamination and passivation of pipelines or secondary circuit components. It can be concluded that a longer passivation time leads more to magnetite fraction in the corrosion products composition.

Differences in hematite and magnetite content in corrosion layers taken from hot and cold collectors at SG11 in 2004 show, that there is a significantly lower presence of magnetite in case of hot collector. This fact can be derived from 2 parallel factors: (i) difference in temperature (about 298°C - HC) and (about 223°C - CC) and mostly due to (ii) higher dynamic of secondary water flowing in the vicinity of hot collector, which high probably removes the corrosion layer away from the collector surface.

With the aim to summarize our results in the form suitable for daily use in the operational conditions a summarized figure was created (see Fig. 16). Corrosion products phase composition (limited on magnetite and hematite only) is presented in form of circular diagrams.

Basically, the corrosion of new feed water pipelines system (from austenitic steel) in combination with operation regimes (as it was at SG35 since 1998) goes to magnetite. In samples taken from positions 5 to 14 (see Fig. 16 - right corner). The hematite presence is mostly on the internal surface of SG body (constructed from "carbon steel" according to GOST20K). Its concentration increases towards the top of the body and is much significant in the seam part of SG where flowing water removes the corrosion layer via erosion better than from the dry part of the internal surface or upper part of pipeline.

The long-term study of phase composition of corrosion products at VVER reactors is one of precondition to the safe operation over the projected NPP lifetime. The long-term observation of corrosion situation by Mössbauer spectroscopy is in favour of utility and is not costly. Based on the achieved results, the following points could be established as an outlook for the next period:

1. In collaboration with NPP-Bohunice experts for operation as well as for chemical regimes, several new additional samples from not studied places should be extracted and measured by Mössbauer spectroscopy with the aim to complete the existing results database.
2. Optimisation of chemical regimes (having in mind the measured phase composition of measured corrosion specimens from past) could be discussed and perhaps improved.
3. Optimisation and re-evaluation of chemical solutions used in cleaning and/or decommissioning processes during NPP operation can be considered.

In connection to the planned NPP Mochovce 3, 4 commissioning (announced officially at 3.10.2008) it is recommended that all feed water pipelines and water distribution systems in steam generators should be replaced immediately before putting in operation by new ones constructed from austenitic steels. The Bohunice design with feed water distribution boxes is highly recommended and it seems to be accepted from the utility side.

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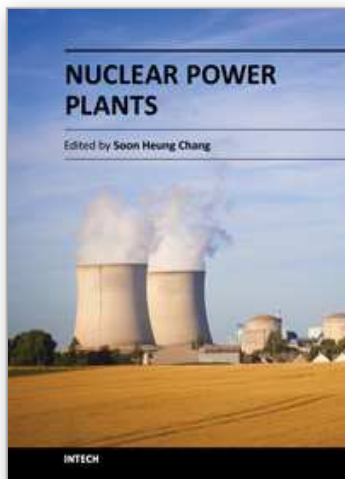
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